

UNITED STATES PATENT OFFICE

STEWART ELMER SEAMAN, OF BUFFALO, NEW YORK, ASSIGNOR TO E. I. DU PONT DE NEMOURS & COMPANY, OF WILMINGTON, DELAWARE, A CORPORATION OF DELAWARE

PROCESS OF PRODUCING CELLULOSE

No Drawing.

Application filed January 9, 1930. Serial No. 419,729.

This invention relates to the manufacture of cellulose pulp and more particularly to an alkaline, neutral or non-acid process of manufacturing cellulose pulp by the use of aqueous ammonia and ammonium salts.

Example I

The following is given as an example of one method of purifying cotton linters or hull fiber or a mixture of the two, as second cut cotton linters, for instance, government gradings, #6 or #7, or certain commercial hull fiber. The cotton fiber is charged to the usual vertical type of digester used for that purpose and seven parts by weight of a cooking liquor composed of approximately 0.7% concentration (NH_3 basis) is added for each part by weight of cotton. The temperature of the digester is then raised to approximately 320°F . and maintained there for four hours after which the charge is blown to the wash tank. The blow tank, pit or wash tank is in the present process provided with a tight cover and is piped to the ammonia recovery system. The ammonia may be recovered direct from the digester upon completion of the cooking or in order to prevent the gas pressure from rising, the ammonia may be conducted to scrubbing towers as will be readily understood. The ammonia may also be recovered from spent cooking liquors or wash waters by adding enough lime to replace the ammonia and then driving off the ammonia by heating and recovering it in towers. With a revolving or tumbling type of digester the ratio of cooking liquor may be reduced. In some instances as little as 2.5 parts of liquor to one part of cotton may be used with consequent saving of ammonia. The viscosity of the product will be increased by lowering the cooking temperature or shortening the cooking time. The unbleached lint may then be bleached and finished in the usual manner but less bleach will be required.

Example II

When purifying a number five grade of linters (mill run) for producing a high viscosity pulp suitable for acetylation or nitration with minimum of resistant fibres, the lint is first thoroughly washed to remove dirt and hull particles after which it is charged to the digester with seven parts of cooking liquor composed of 0.3% ammonia (NH_3)

This invention has as an object, a process for the production of cellulose pulp which results in a better yield, a higher percentage of alpha cellulose and a whiter color than that resulting from the processes now used involving the usual alkaline or neutral alkali salt treatments. A still further object is the provision of a purification process in which the recovery of the alkali may be more economically effected than when caustic soda and other sodium salts are used. Other objects will appear hereinafter.

These objects are accomplished by the following invention in which cellulose fiber from various sources is digested with ammonia or ammonium salts or ammonia and ammonium salt or a mixture of ammonium salts, under conditions of temperature and concentration most favorable for the production of high grade pulp, and in which the ammonia may be recovered for further utilization as a cooking agent.

The material utilized for the production of high grade cellulose pulp in accordance with the present invention may be crude cellulose such as cotton linters, hull fiber, wood, chips, bagasse, cornstalks, esparto, straw, flax, jute, ramie, hemp, etc., either unbleached or partly or completely bleached. Ammonia may be used alone as the pulping reagent but for many purposes and with cellulose material from some origins I find that certain ammonium salts or mixtures thereof or ammonia and an ammonium salt give desirable results.

Such reagents are:

1. Ammonium sulphite
2. Ammonia and ammonium sulphite
3. Ammonia and ammonium sulphate
4. Ammonia and ammonium carbonate
5. Ammonia and ammonium sulphide
6. Ammonium sulphite and ammonium sulphide

basis) with 1.7% ammonium carbonate and 0.5% rosin and is cooked for three hours at approximately 230° F. after which the cooking liquor is blown off through a perforated plate and the pulp in the digester, is further boiled for one hour with water and is then drained and given a cold water wash. The pulp is then dumped from the revolving digester or may be blown out by steam pressure. It is then bleached, washed and dried as desired.

It is to be understood however, that in the above and following examples the conditions may be varied, as understood by those skilled in the art, in accordance with the different raw materials and with the different types of digesters and with the characteristics desired in the product. In the purification of cotton linters or hull fiber it is usually desired to get the highest possible alpha cellulose content with the minimum soda solubility, ash, ether extract with the whitest color, together with some predetermined viscosity. When prepared for dynamite or smokeless powder the purified cotton is not usually bleached and whiteness therefore is not a factor. When purifying however, for rayon, lacquer, safety glass, plastics etc., brilliant whiteness is wanted. For dynamite the cellulose viscosity must be high, for lacquer preferably low, for plastics medium and for these reasons it must be borne in mind that the example here submitted can be varied by one skilled in the purification of linters when preparing pulp for any one of the particular products mentioned.

Example III

To produce a high grade of so-called soda pulp of improved color, yield and alpha cellulose content, spruce, western hemlock, poplar, cotton wood, white maple, gum or other woods are chipped in the usual manner and charged in this case to the tumbling end for end type of soda or sulphate digester. Five parts of cooking liquor composed of approximately two percent ammonia (NH₃ basis) to each part by weight of the wood are added to the digester and the charge cooked for seven hours at approximately 330° F. including about two hours for bringing the charge to that temperature. The quantity of liquor to pulp is varied based on the percentage of moisture in the chips but the percent of ammonia to wood will remain approximately constant. Different species of wood will require different quantities of ammonia, for example, spruce may be cooked with about 1.5% ammonia (NH₃ basis). After blowing the digester the pulp may be washed, bleached and dried in the usual manner.

Example IV

A variation in the procedure referred to in Example III for producing a high grade

so-called soda pulp with further improvement in color and yield may be had by cooking the chips with five parts of a cooking liquor composed of about 4.5% ammonium sulphite slightly on the alkaline side for six hours at a temperature of approximately 330° F. The quantity of liquor to pulp may be varied based on the per cent of moisture in the chips but the per cent of ammonium sulphite to the wood will remain approximately constant. After blowing the digester, the pulp may be washed, bleached and dried in the usual manner, but bleach requirements will be reduced over the process described in Example III.

Example V

To produce a pulp of maximum strength, particularly for paper and similar to that known as kraft but of distinctly improved color, wood chips or other cellulose base material is charged to the usual type of digester with 5 parts of a cooking liquor consisting of approximately 2% ammonia (NH₃ basis) with 2% ammonium sulphide and cooked for two hours at approximately 330° F. after which the charge is blown, washed and dried in the usual manner.

Example VI

To produce a high grade pulp of improved color, yield and alpha cellulose content from cornstalks, bagasse and similar fibrous materials, the pith is first separated mechanically from the fibrous material by any of the usual means such as a shredder and duster, is washed to remove sugar and after charging the disintegrated fibrous matter to a digester, six parts of a cooking liquor composed of approximately 4% ammonium sulphite slightly on the alkaline side is added and cooked for four or five hours at approximately 280° F. after which the digester is blown and the pulp is washed, bleached and dried in the usual manner as desired. Stalk, raw cellulose and similar materials require varying treatments and often benefit in the cooking by the addition of an excess of ammonia and addition of ammonium sulphide and in the same procedure just mentioned there may be substituted six parts of a liquor composed of 4% ammonium sulphite with 9.7% ammonium sulphide and 9.16% ammonia (NH₃ basis).

Example VII

To produce a pulp particularly high in alpha cellulose with maximum yield and excellent whiteness from relatively high ligno cellulose base raw materials, such as wood, the chips are preferably cooked with ammonium acid sulphite and sulphurous acid, the aqueous cooking liquor containing 3.5% of ammonium bisulphite and 1.5% sulphurous acid, raising the temperature gradually to about 230° F. when cooking spruce or to

250° F. when cooking western hemlock in 2 to 3 hours and then further gradually raised to not over 320° F. in four hours and the temperature held for one hour and when tests indicate the cook to be completed, it is then blown with the usual SO₂ recovery and in addition the NH₃ may be recovered from the spent sulphite liquors. The pulp is washed then submitted to a secondary cooking preferably in a rotating tumbling end to end type of digester with a solution consisting of seven parts of approximately 0.3% ammonia (NH₃ basis) to each part of pulp for ninety minutes at approximately 280° F. The temperature may be reduced to the boiling point or even slightly less dependent upon the viscosity wanted as the alpha cellulose content will not be materially improved having already been raised about as high as it can be made from wood pulp. The digester is then blown and the pulp is washed and bleached with the small amount required and dried in the usual manner desired.

The last example is the most desired process for very high alpha content wood cellulose of outstanding whiteness particularly for the production of nitro and acetate cellulose products, cupra ammonium and viscose rayon, etc., and it is mentioned that the acid pretreatment may be accomplished by other ratios of ammonium bisulphite and sulphurous acid in the mixture and the pressures, temperatures, and time of treatment may be varied or even the more broadly known sulphite processes with lime or dolomite or soda base bisulphite cooks may be used and the secondary treatment may be modified by substituting the neutral ammonium sulphite, or ammonium sulphite and ammonia, with or without ammonium sulphide, or with ammonium carbonate or ammonium carbonate and ammonia, or other mixtures of ammonium base salts and ammonia. A treatment with a small amount of bleach liquor or chlorine water of the pulp resulting from the first step acid treatment will result in certain improvements in whiteness and such treatment may be employed when desired.

In each of the foregoing examples the ammonia may be recovered as more specifically referred to in connection with Example I.

The pulp produced by the process of the present invention is high in alpha cellulose and is suitable for the production of viscose rayon, films or the like, cupra ammonium rayon, nitro cellulose or cellulose acetate solutions, and for the production of lacquers, plastics, explosives and for various grades of paper. The brilliancy and whiteness of the product makes it especially desirable for rayon, lacquer and safety glass.

The process of the present invention accomplishes a more complete removal of the non-alpha cellulose matter, producing a pulp of greater purity with a brighter color and

higher yield than that made when employing other alkalies as a base. This process has also the outstanding advantage over fixed alkali processes in that the alkaline base may be recovered readily because of its ready conversion into a gas by replacement from its compounds. The ammonia is readily recoverable with a cheap base like lime and is recovered in purer state with less loss and at cheaper cost with less costly equipment than is possible the recovery of the base when other alkalies are used. The cooking time may also be shortened by taking advantage of the increased pressure due to the formation of ammonia gas upon heating.

As many apparently widely different embodiments of this invention may be made without departing from its spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended patent claims.

I claim:

1. A process of purifying cellulose which comprises cooking vegetable fibrous material with an aqueous solution comprising a mixture of ammonium sulphite and ammonium sulphide.
2. A process of purifying cellulose which comprises cooking vegetable fibrous material with an aqueous solution comprising a mixture of ammonium sulphite, ammonium sulphide and ammonia.
3. A process of purifying cellulose which comprises cooking vegetable fibrous material with an aqueous bisulphite solution and sulphurous acid removing the bisulphite solution and cooking further with aqueous ammonia.
4. A process of purifying cellulose which comprises cooking vegetable fibrous material with an aqueous bisulphite solution and sulphurous acid removing the bisulphite solution and cooking further with an aqueous solution of an ammonia compound.
5. A process of purifying cellulose which comprises cooking vegetable fibrous material with an aqueous bisulphite solution and sulphurous acid removing the bisulphite solution, and cooking further with an aqueous solution containing ammonia and an ammonium salt.
6. A process of purifying cellulose which comprises cooking vegetable fibrous material with an aqueous bisulphite solution and sulphurous acid removing the bisulphite solution and cooking further with an aqueous solution of ammonium sulphite.
7. A process of purifying cellulose which comprises cooking vegetable fibrous material with an aqueous bisulphite solution and sulphurous acid removing the bisulphite solution and cooking further with an aqueous solution comprising a mixture of ammonia and ammonium sulphite.

8. A process of purifying cellulose which comprises cooking vegetable fibrous material with an aqueous bisulphite solution and sulphurous acid removing the bisulphite solution and cooking further with an aqueous solution comprising a mixture of ammonia, ammonium sulphite and ammonium sulphide. 5
 9. A process of purifying cellulose which comprises cooking vegetable fibrous material with a liquor consisting of a mixture of ammonium bisulphite and sulphurous acid, removing the liquor and cooking further with aqueous ammonia. 10
 10. A process of purifying cellulose which comprises cooking vegetable fibrous material with a liquor consisting of a mixture of ammonium bisulphite and sulphurous acid, removing the liquor and cooking further with an aqueous solution of an ammonia compound. 15
 11. A process of purifying cellulose which comprises cooking vegetable fibrous material with a liquor consisting of a mixture of ammonium bisulphite and sulphurous acid, removing the liquor and cooking further with an aqueous solution comprising a mixture of ammonia and an ammonium salt. 20
 12. A process of purifying cellulose which comprises cooking vegetable fibrous material with an aqueous bisulphite solution and sulphurous acid, at least partially bleaching the cellulose before further re-cooking, removing the bisulphite solution and cooking further with aqueous ammonia. 25
 13. A process of purifying cellulose which comprises cooking vegetable fibrous material with an aqueous bisulphite solution and sulphurous acid, at least partially bleaching the cellulose before further re-cooking, removing the bisulphite solution and cooking further with aqueous ammonia. 30
 14. A process of purifying cellulose which comprises cooking vegetable fibrous material with an aqueous bisulphite solution and sulphurous acid, at least partially bleaching the cellulose before further re-cooking, removing the bisulphite solution, and cooking further with an aqueous solution containing ammonia and an ammonium salt. 35
 15. A process of purifying cellulose which comprises cooking vegetable fibrous material with an aqueous bisulphite solution and sulphurous acid, at least partially bleaching the cellulose before further re-cooking, removing the bisulphite solution and cooking further with an aqueous solution of ammonium sulphite. 40
 16. A process of purifying cellulose which comprises cooking vegetable fibrous material with an aqueous bisulphite solution and sulphurous acid, at least partially bleaching the cellulose before further re-cooking, removing the bisulphite solution and cooking further with an aqueous solution comprising a mixture of ammonia and ammonium sulphite. 45
 17. A process of purifying cellulose which comprises cooking vegetable fibrous material with an aqueous bisulphite solution and sulphurous acid, at least partially bleaching the cellulose before further re-cooking, removing the bisulphite solution and cooking further with an aqueous solution comprising a mixture of ammonia, ammonium sulphite and ammonium sulphide. 50
 18. A process of purifying cellulose which comprises cooking vegetable fibrous material with an aqueous bisulphite solution and sulphurous acid, at least partially bleaching the cellulose before further re-cooking, removing the bisulphite solution and cooking further with an aqueous solution of ammonium sulphide. 55
 19. A process of purifying cellulose which comprises cooking vegetable fibrous material with a liquor consisting of a mixture of ammonium bisulphite and sulphurous acid, at least partially bleaching the cellulose before further re-cooking, removing the liquor and cooking further with aqueous ammonia. 60
 20. A process of purifying cellulose which comprises cooking vegetable fibrous material with a liquor consisting of a mixture of ammonium bisulphite and sulphurous acid, at least partially bleaching the cellulose before further re-cooking, removing the liquor and cooking further with an aqueous solution of an ammonia compound. 65
 21. A process of purifying cellulose which comprises cooking vegetable fibrous material with a liquor consisting of a mixture of ammonium bisulphite and sulphurous acid, at least partially bleaching the cellulose before further re-cooking, removing the liquor and cooking further with an aqueous solution comprising a mixture of ammonia and an ammonium salt. 70
 22. The process of obtaining cellulose from a fibrous vegetable material which comprises cooking the fibrous vegetable material in an acid bath and thereafter cooking the fibrous material with an aqueous solution of an ammonia compound. 75
 23. The process of obtaining cellulose from a fibrous vegetable material which comprises cooking the fibrous vegetable material with an acid solution, bleaching, and thereafter cooking with an aqueous solution of an ammonia compound. 80
- In testimony whereof, I affix my signature.
STEWART E. SEAMAN.